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(54) Title: CELLULOSIC SHEET MATERIAL

(57) Abstract

There is disclosed a sheet of cellulosic material comprising a base material which contains hydrophobic contaminants, and a coating formed from a coating composition comprising an aqueous suspension containing a pigment, an adhesive and a small amount, preferably in the range of from about 0.2 % to about 2 % by weight, based on the weight of the dry pigment, of a surfactant. The surfactant is preferably a non-ionic surfactant having an HLB value in the range 8 to 14.

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CELLULOSIC SHEET MATERIAL

The invention relates to cellulosic sheet material, for example paper or paperboard, prepared from a base material which has dispersed within it particles of hydrophobic contaminating materials.

It is often found that sheet materials formed from cellulosic fibre compositions contain within them a small, but significant, proportion of hydrophobic contaminants which tend to be dispersed throughout the sheet material in the form of small particles or globules. These particles or globules are usually referred to in the paper making art as "stickies" or "hickies". A sheet-forming composition generally comprises a dilute suspension of cellulosic fibres and, usually, a proportion of inorganic filler particles which are added to improve the brightness and opacity of the sheet material which is formed from the composition. The incidence of hydrophobic contaminants is often especially high when the mixture used as the source of cellulosic fibres contains a high proportion of recycled waste paper. Also, some types of tree which are used as a source of cellulosic fibres for sheet forming processes are especially rich in hydrophobic substances: eucalyptus is an example of such a tree.

In order to apply a good quality printed image to the surface of a cellulosic sheet material, it is generally advantageous to prepare the sheet material by coating at least one surface thereof with a composition which gives the coated material a uniform smooth and level surface on to which the printed image may be applied. A typical coating composition generally comprises an aqueous suspension of a pigment, which is usually, but not always, white in colour, and an adhesive. A dispersing agent for the pigment is generally also required, and other additives to modify the rheological or optical properties of the composition

may be included. The most commonly used pigments in paper coating compositions include natural and calcined kaolinitic clays, calcium carbonate, calcium sulphate, barium sulphate, titanium dioxide and talc.

When a coating composition of the type described above is applied to the surface of a sheet material which contains "stickies", it is usually found that the coating composition will not wet and adhere to the hydrophobic spots in the material caused by the stickies, and the resultant coating, after drying, shows a number of uncoated spots. As the stickies are often dark in colour, they remain clearly visible in the coated sheet material, and give it an unattractive appearance.

Paperboard is generally made from relatively low quality pulp and tends to be darker in colour and rougher in texture than good quality printing paper. However, for packaging purposes, it is often required to apply a printed image to at least one surface of the paperboard. Paperboard may be made by forming a relatively thick and heavy layer of cellulosic fibres on the wire mesh belt of a sheet forming machine, but usually it is preferred to manufacture paperboard by laminating together several layers of thinner sheet material. The inner layers tend to be of relatively low quality cellulosic material, and sheets of better quality material may be used to form the outer layers. However, it is usually necessary to coat even the sheet material used for the outer layers if a printed image of acceptable quality is to be applied. Also, even the sheet material used for the outer layers of paperboard may contain stickies which repel aqueous coating composition, with the result that the coating does not adhere to these locations, and unsightly spots remain in the coated surface.

In the prior art, the problem of coating a cellulosic sheet material containing "stickies" has been tackled by either (i) applying a white liner material comprising paper usually of good quality onto the appropriate surface of the sheet material and coating the liner material; such a process for coating sheet material is expensive; or (ii) applying a conventional coating and accepting that the quality of the final product is limited by appearance of defects caused by the stickies.

According to the present invention there is provided a method of coating a sheet of cellulosic material with a coating composition comprising an aqueous suspension of pigment material and an adhesive, wherein the sheet of cellulosic material contains one or more defect spots visible to the naked eye comprising one or more hydrophobic contaminants, characterised in that a wetting agent having hydrophobic and hydrophilic moieties is applied to at least one surface of the sheet to enable the spot or spots to be contacted by a water containing composition and the said surface is coated by the coating composition to form a coating which is uniform and substantially free of uncoated spots.

The wetting agent if preferably applied to the said surface in a water containing composition. Such composition may be the said coating composition or, alternatively, a material applied as an intermediate layer on which the said coating material is subsequently deposited, eg. after drying. Such an intermediate layer (apart from the surfactant) may for example be one of the intermediate coatings applied in the prior art, eg. a so called "wash pre-coat", eg. comprising a binder, eg. latex or starch, in water optionally together with a coarse pigment material generally in a water based composition containing less than 50% by weight solids.

The said wetting agent may for example comprise a known wetting agent, eg. a surfactant or surface active agent.

The said wetting agent may for example be applied to the sheet of cellulosic material in an amount ranging from 0.2% to 2% by weight based upon the dry weight of pigment or pigments present in the added coating composition.

There may, for example, be at least two of the said defect spots present in each $0.01m^2$ unit of surface area of the sheet of cellulosic material treated. For example, a sheet of paperboard of dimensions 10cm by 20cm may have four or five spots on its surface.

The said defect spot or spots may comprise one or more spots which are dark in colour compared to the defect-free areas of the treated surface of the sheet of cellulosic material.

The said defect spot or spots may for example be spots which have an average diameter of at least 100 micrometres (100μm). The hydrophobic material contained within the defect spots may for example comprise fats or fatty acids or mixtures thereof.

The sheet of cellulosic material treated by the method of the present invention may comprise a paper product, eg. a sheet of paper or a paper board, eg. manufactured in a known way, eg. as described hereinbefore. The present invention is especially suitable for coating sheets of cellulosic materials wherein the presence of stickies is known to be common, eg. in paper products produced from pulps derived from large amounts eg. 50% to 100% of waste paper or in products produced from pulps derived from certain tree types, eg. trees from tropical and sub-tropical regions which may product large amounts of organic solvent extractives.

Where the said wetting agent comprises a surfactant compound or composition, the surfactant may be of the anionic, cationic, non-ionic or amphoteric type. Surfactants of the non-ionic type are preferred because, in general, they have a smaller tendency to generate foam in the coating composition than the other types. A surfactant of the non-ionic type

having a hydrophile/lipophile balance (HLB) value of at least 8, especially in the range of from 8 to 14 is especially advantageous because it provides suitable spot wetting without excessive detergent or solvent activity.

The coating composition employed in the method according to the present invention may comprise a known paper coating composition which (apart from the wetting agent), may be made in one of the ways well known to those skilled in the art.

The pigment material employed in the coating composition may comprise a kaolin clay in its natural or hydrous state or a kaolin clay which has been calcined to drive off chemically combined water. Alternatively or in addition, the pigment may comprise calcium carbonate, calcium sulphate, barium sulphate, talc, satin white or titanium dioxide. A mixture of two or more pigment materials is frequently desirable. The pigment or pigments are conveniently first mixed with water containing a dispersing agent to form a relatively concentrated suspension to which other components of the coating composition are added. Suitable dispersing agents are well known per se and include water soluble salts of polysilicic acids, water soluble condensed phosphate salts and water soluble salts of poly (acrylic acid), of poly (methacrylic acid) and of polymers of related ethylenically unsaturated acids and blends and copolymers of these species. The quantity of the dispersing agent used may be in the range of from 0.05% to 1% by weight, based on the dry weight of the pigment material(s).

The adhesive employed in the coating composition may comprise an adhesive of the carbohydrate type, such as a starch or one of the various derivatives of starch and cellulose, of the protein type, such as casein, or of the latex type, such as latices of styrene butadiene rubber or of various acrylic polymers. A mixture of two or more of these types of adhesive may be used. Generally, the amount of adhesive used is in the range of from about 4% to about 20% by weight, based on the dry weight of pigment material in the

composition. Other known optional additives may be included in the composition.

Conveniently, where the surfactant is employed in the coating composition, the surfactant is added to the composition after all the other ingredients have been added, but it is also possible to add the surfactant at an earlier stage in the preparation of the composition.

After application of the coating material the coated sheet of cellulosic material may be dried in a known way, eg. by infra-red heating and/or evaporative drying in warm air.

The thickness of the coating composition applied will depend upon the make-up of the coating composition, the base material being coated, and the nature of the defect spots (eg. darkness of the spots). The coating composition may be added to the sheet of cellulosic material to be coated in a manner well known in the art. More than one coating layer may be applied. One or more of these may be one of the intermediate pre-coatings referred to above. Alternatively, or in addition, multiple coatings of the final coating composition may be made. For example a first coating layer may be applied and allowed to dry and then a second coating layer may be applied and then allowed to dry. Overall, the amount of the coating composition applied may be such that the weight per unit area after drying of the coating composition is at least $5gm^{-2}$ (grammes per metre squared) desirably at least $10gm^{-2}$.

According to the present invention in a second aspect there is provided a coated sheet of cellulosic material which has been produced by the method according to the first aspect.

Beneficially, the present invention allows the problem of coating sheets of cellulosic material containing defect spots comprising hydrophobic material or "stickies" as described hereinbefore to be solved without using an expensive additional paper liner material as described hereinbefore.

Paper coating compositions containing surfactants for specific purposes have been reported in certain references in the prior art. For example, the article "Some aspects of

coating with surfactants upon quality and offset printability" by J.F.Lafaye, J.P.Maume, G.Gervason and P.Piette, published in the TAPPI Proceedings of the 1987 Coating Conference, pages 107-115, describes experiments using specific compositions of this type. However, the use of a surfactant in conjunction with a coating composition to solve the problem of coating sheets of cellulosic material containing defect spots comprising "stickies" or hydrophobic material, and the benefits arising therefrom, have not been suggested in the prior art.

Embodiments of the present invention will now be described by way of example only with reference to the accompanying drawing which is a representation of the surfaces of three sheets of paperboard showing the effect of treatment in accordance with the present invention.

The invention is illustrated by the following Examples.

Example 1

Coating compositions were prepared according to the following general formulation:

Ingredient	Parts by weight
Hydrous kaolin clay	90
Calcined kaolin clay	10
Latex adhesive (polymer solids)	11
Sodium carboxymethyl cellulose	1
Surfactant	1

The hydrous clay was an English kaolin clay having a particle size distribution such that 80% by weight of the particles had an equivalent spherical diameter smaller than 2μm. This clay was introduced into the composition in the form of an aqueous suspension containing 68% by weight of the dry clay and 0.3% by weight, based on the weight of dry clay, of a sodium polyacrylate dispersing agent and 0.08% by weight, based on the weight of dry kaolin, of sodium hydroxide.

The calcined clay was prepared by calcining a fine kaolin from Georgia, U.S.A. and had a particle size distribution such that 90% by weight of the particles had an equivalent spherical diameter smaller than 2μm. This clay was introduced into the composition in the form of an aqueous suspension containing 49% by weight of the dry calcined kaolin and 0.1% by weight, based on the weight of dry calcined kaolin, of a sodium polyacrylate dispersing agent.

The two clay suspensions were blended in a laboratory mixer in the proportions of 90 parts by weight of dry hydrous clay to 10 parts by weight of dry calcined clay. The latex adhesive, which contained 50% by weight

of a carboxylated styrene-butadiene copolymer, was then mixed into the blended clay suspension. The sodium carboxymethyl cellulose was then added to the stirred mixture in the form of a 10% by weight solution in water. Sufficient of a 10% by weight solution of sodium hydroxide was then added to raise the pH to 8.5. Finally the surfactant was mixed in with stirring.

The following surfactants were used:

Anionic:-

A1 - Sodium dodecylbenzenesulphonate

A2 - Sodium dioctylsulphosuccinate (AEROSOL OT™)

Cationic:-

Am1 - 1-hydroxyethyl-2-heptadecenyl imidazoline (REWOPON IMOA™)

C1 - Polypropoxyldiethylmethylammonium chloride (EMCOL CC9™)

Non-ionic:-

N1-N3 - Alcohol ethoxylates of formula $R(OCH_2CH_2)_nOH$

Type	R	n	HLB	Trade Name
N1	C_9-C_{11}	2.5	8.1	DOBANOL 91-2.5
N2	C_9-C_{11}	6	12.5	DOBANOL 91-6
N3	C_9-C_{11}	8	13.7	DOBANOL 91-8

Each composition was diluted with sufficient water to give a low shear viscosity as measured using a Brookfield Viscometer [at 100rpm using Spindle No.3 of 350mPa.s. In the case of the compositions containing all of the surfactants except for Am1 the solids content of the composition was 51% by weight. Surfactant Am1 caused thickening of the composition and, in this case, the solids content was reduced to 41% by weight to give the required low shear viscosity level.

The compositions were coated onto sheets of paperboard each measuring 10 x 20cm using a No.10 wire

wound coating bar. Each composition was coated on to 10 of the small sheets. The paperboard was light brown in colour and each sheet had up to 4 or 5 visible spots which were caused by the presence of stickies. After drying, the average weight of coating on the test sheets was found to be $10g.m^{-2}$.

In the case of each of the compositions it was found that the coating had adhered well to all parts of the surface of the paperboard, including the locations of the stickies, and the defect spots were concealed by the coating.

As a comparison, further sheets of the paperboard were coated with a composition which was prepared in exactly the same way as described above, but containing no surfactant. The coated sheets after drying showed that the coating had not adhered to the surface of the paperboard at the locations of the stickies, and the spots remained visible.

The accompanying Figure shows photographic images of the surfaces of 1 the uncoated brown paperboard, 2 the paperboard which had been coated with a composition containing no surfactant, and 3 the paperboard which had been coated with the composition containing surfactant N3. It will be noted that, although dark spots are visible in the uncoated paperboard 1, and in coated paperboard 2, coated paperboard 3 shows no visible spots.

Example 2

Coating compositions were prepared as described above containing surfactants A2 and N3. In this case the complete compositions were diluted before coating with sufficient water to reduce the low shear viscosity, as

measured with a Brookfield Viscometer at 100rpm using Spindle No.5, to 1600mPa.s. The compositions were coated on to the same light brown paperboard as was described in Example 1 using a laboratory paper coating machine of the type described in British Patent Specification No. 1032536 at a speed of 400m.min^{-1}, a blade angle of 45° and at a blade deflection which was adjusted to give a coat weight of 14g.m^{-2}.

As a comparison a composition prepared in exactly the same way but containing no surfactant was coated on to the base paperboard in the same manner.

The samples of paperboard which had been coated with the compositions containing the surfactants showed good coverage of the whole surface of the paperboard with no visible spots, whereas, in the case of the sample of the paperboard which had been coated with the composition containing no surfactant, the coating had not adhered to the surface of the paperboard at the location of the stickies, and dark spots were still clearly visible.

Example 3

The two previous Examples concern coating compositions containing kaolin clay as the sole coating pigment. This further Example shows the effect of using a coating composition in which a proportion of the clay is substituted with calcium carbonate. The composition was prepared according to the following general formulation:

Ingredients	Parts by weight
Hydrous kaolin clay	50
Calcium Carbonate	50
Latex adhesive (polymer solids)	12
Sodium carboxymethyl cellulose	1.5
Surfactants	1

The hydrous clay was an English kaolin clay having a particle size distribution such that 80% by weight of the particles had an equivalent spherical diameter

smaller than 2μm. This clay was introduced into the composition in the form of an aqueous suspension containing 68% by weight of the dry clay and 0.3% by weight, based on the weight of the dry clay, of a sodium polyacrylate dispersing agent and 0.8% by weight, based on the weight of dry clay, of sodium hydroxide.

The calcium carbonate had a particle size distribution size such that 90% by weight of the particles had a equivalent spherical diameter smaller than 2μm. This carbonate was introduced into the composition in the form of an aqueous suspension containing 75% by weight of the dry calcium carbonate and 0.6% by weight, based on the weight of dry calcium carbonate, of a sodium polyacrylate dispersing agent.

The two pigment suspensions were blended in a laboratory mixer in the proportions of 50 parts by weight of the dry hydrous clay to 50 parts by weight of calcium carbonate. The latex adhesive, which contained 50% by weight of a carboxylated styrene - butadiene copolymer, was then mixed into the blended suspension. The sodium carboxymethyl cellulose was then added to the stirred mixture in the form of a 10% by weight solution in water. Sufficient of a 10% by weight solution of sodium hydroxide was then added to raise the pH to 8.5. Finally the surfactant was mixed in with stirring.

As in Example 1 the composition was diluted with sufficient water to give a low shear viscosity as measured using a Brookfield Viscometer [at 100rpm using Spindle No. 3] of 350mPa.s. The solids content of the composition containing surfactant was 10% by weight.

The composition was coated onto sheets of light brown paperboard using exactly the same method as described in Example 1. As a comparison a composition prepared in the same way but containing no surfactant was coated onto the base paperboard in the same manner.

The samples of paperboard which had been coated with

the composition containing the surfactant showed good coverage of the whole surface of the paperboard with no visible spots, whereas, in the case of the sample of the paperboard which had been coated with the composition containing no surfactant, the coating had not adhered to the surface of the paperboard at the location of the stickies, the dark spots were still clearly visible.

Claims

1. A method of coating a sheet of cellulosic material with a coating composition comprising an aqueous suspension of pigment material and an adhesive wherein the sheet of cellulosic material contains one or more defect spots visible to the naked eye comprising one or more hydrophobic contaminants, characterised in that a wetting agent having hydrophobic and hydrophilic moieties is applied to at least one surface of the sheet to enable the spot or spots to be contacted by a water containing composition and the said surface is coated by the coating composition to form a coating which is uniform and substantially free of uncoated spots.

2. A method as claimed in claim 1 and wherein the wetting agent is applied to the said surface in a water containing composition.

3. A method as claimed in claim 2 and wherein the water containing composition comprises an intermediate pre-coating layer on which the said coating composition is deposited optionally after drying of the pre-coating layer.

4. A method as claimed in claim 1 or claim 2 and wherein the wetting agent is added to the said surface together with the said coating composition as a single composition.

5. A method as claimed in claim 1, 2, 3 or 4 and wherein the wetting agent is present in an amount of from 0.2% to 2.0% by weight based upon the dry weight of pigment or pigment materials present in the coating composition.

6. A method as claimed in any one of the preceding claims and wherein the wetting agent comprises a surfactant of the anionic type or of the cationic type or of the non-ionic type or of the amphoteric type.

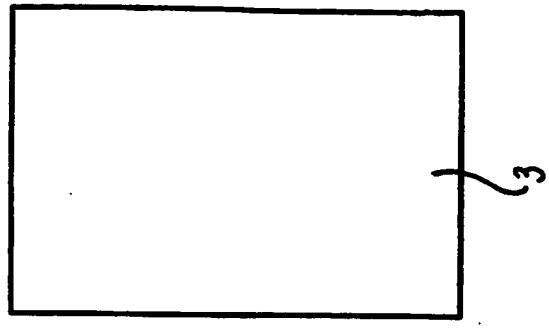
7. A method as claimed in claim 6 and wherein the surfactant is of the non-ionic type having a hydrophile/lipophile balance value in the range of from 8 to 14.

8. A method as claimed in any one of the preceding claims and wherein the coating composition is added to the said

surface in more than one coating application.

9. A method as claimed in any one of the preceding claims and wherein the coating composition is dried after application to the surface of the sheet of cellulosic material and the weight per unit area after drying of the coating formed from the coating composition is at least 5 grammes per metre squared.

10. A coated sheet of cellulosic material which is the product of the method claimed in any one of claims 1 to 9.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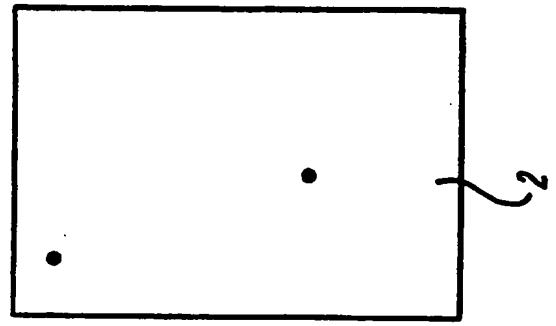
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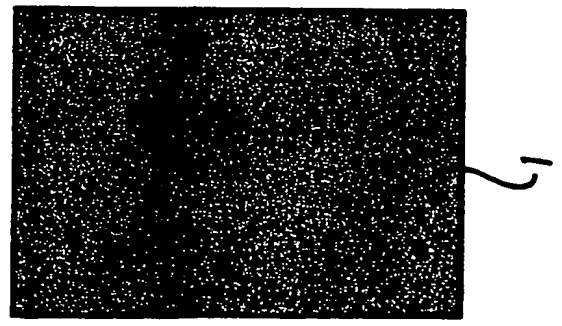
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INTERNATIONAL SEARCH REPORT

Inter ıal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21H19/72 D21H19/46 D21H19/82

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 923 566 A (SHAWKI SHAMEL M ET AL) 8 May 1990 see the whole document	1,10
A	EP 0 171 168 A (ENGELHARD CORP) 12 February 1986 see the whole document	1,4-7,9, 10
A	EP 0 377 283 A (ECC INT LTD) 11 July 1990 see claims 8-10	1

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☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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.formation on patent family members

Inter nal Application No
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